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thiosemicarbonato) bis[acetonitrilecopper(I)]  
bis(tetrafluoroborate)

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**Bis( $\mu$ -thiophene-2-carbaldehyde  
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**Robert D. Pike, Austin B. Wiles and Tristan A. Tronic**

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## Bis( $\mu$ -thiophene-2-carbaldehyde thiosemi-carbazonato)bis[acetonitrilecopper(I)] bis(tetrafluoroborate)

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### Key indicators

Single-crystal X-ray study

$T = 100$  K

Mean  $\sigma(\text{C}-\text{C}) = 0.011$  Å

$R$  factor = 0.045

$wR$  factor = 0.111

Data-to-parameter ratio = 13.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

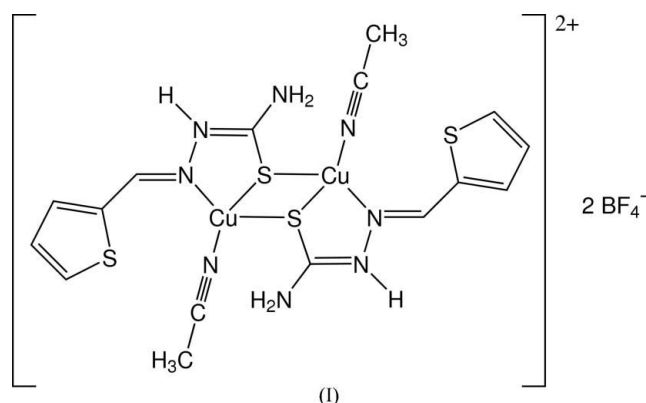
The title compound,  $[\text{Cu}_2(\text{C}_6\text{H}_7\text{N}_3\text{S}_2)_2(\text{C}_2\text{H}_3\text{N})_2](\text{BF}_4)_2$ , is a dimer with a central  $\text{Cu}_2\text{S}_2$  core resulting from thiosemicarbazone sulfur bridging. Both Cu–TCT units (TCT is the thiophene-2-carboxaldehyde thiosemicarbazone anion) are roughly planar and are parallel to one another and perpendicular to the  $\text{Cu}_2\text{S}_2$  plane.

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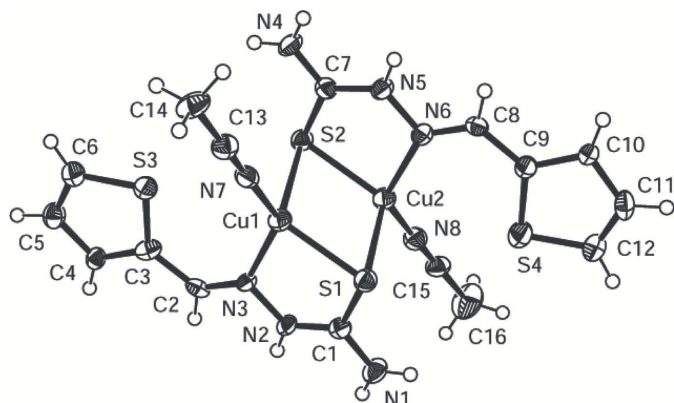
### Comment

As part of a study of thioamide complexes of copper(I), the title compound,  $[\text{Cu}_2(\text{TCT})_2(\text{NCMe})_2](\text{BF}_4)_2$ , (I), was prepared and its crystal structure is presented here.



Compound (I) crystallizes in the orthorhombic space group  $Pca2_1$ . Each  $\text{Cu}^{\text{I}}$  center is chelated by a TCT ligand (TCT is the thiophene-2-carboxaldehyde thiosemicarbazone anion) in a similar fashion to that of the previously known TCT complexes *trans*-Ni(TCT)<sub>2</sub> (Garcia-Tojal *et al.*, 2001), *trans*-Cu(TCT)<sub>2</sub> (Garcia-Tojal *et al.*, 1999), PhHg(TCT) (Lobana *et al.*, 2001) and *cis*-Fe(CO)<sub>2</sub>(TCT)<sub>2</sub> (Hong *et al.*, 2004). In contrast with these species, but in keeping with typical  $\text{Cu}^{\text{I}}$  behavior, the two  $\text{Cu}^{\text{I}}$  centers are bridged by the thiosemicarbazone S atoms to form a rhomboid dimer. As is the case with the previously known complexes, the thiophene S atoms fail to coordinate, with  $\text{Cu}1 \cdots \text{S}3 = 3.190$  (2) Å. Instead, acetonitrile ligands complete the distorted tetrahedral coordination of each  $\text{Cu}^{\text{I}}$ .

An analysis of the bond angles reveals that most of the angles about the  $\text{Cu}^{\text{I}}$  atoms are near the nominal tetrahedral value. However, the angles within the Cu–TCT metallocyclic ring, *e.g.* N3–Cu1–S1, are acute, and the angles between the acetonitrile and the chelating TCT, *e.g.* N7–Cu1–N3 and N7–Cu1–S1, are large ( $>120^\circ$ ). Thus, the acetonitrile associated with each  $\text{Cu}^{\text{I}}$  center is angled away from the chelating TCT ligand and slightly towards the bridging TCT ligand. The S–Cu–S angles are near the nominal tetrahedral value, but


**Figure 1**

The molecular structure of (I), showing 50% probability displacement ellipsoids. The anions have been omitted for clarity.

the Cu—S—Cu values are  $<75^\circ$ . The chelating (e.g. N3—Cu1—S1) and non-chelating (e.g. N3—Cu1—S2) angles in the current structure are relaxed by about  $2\text{--}7^\circ$  in comparison with the analogous angles in the literature structures cited above. This effect is due to the preference of Cu<sup>I</sup> for quasi-tetrahedral, rather than square-planar or octahedral, geometry.

The Cu1...Cu2 distance of 2.8094 (15) Å indicates a long-range metal–metal interaction. The Cu—S and Cu—N distances within the chelate rings, e.g. Cu1—S1 and Cu1—N3, are within the range found for other M–TCT complexes. The fact that the non-chelate Cu—S distances (e.g. Cu1—S2) are significantly longer than the chelate distances suggests that dimer formation is the weaker effect. Comparison of the chelate Cu—S and Cu—N bonds with those in the Cu<sup>II</sup>–TCT structure (Garcia-Tojal *et al.*, 1999) reveals that those in the current structure are longer by about 0.06 Å, a fact that is consistent with the lesser charge on Cu<sup>I</sup>.

Least-squares planes were calculated for Cu1/S1/N2/N3/C1 (plane *A*, maximum deviation 0.053 Å for atom N3), Cu1/S1/Cu2/S2 (plane *B*, maximum deviation 0.007 Å for all atoms), Cu2/S2/N5/N6/C7 (plane *C*, maximum deviation 0.061 Å for atom S2), C3/C4/C5/C6/S3 (plane *D*, maximum deviation 0.004 Å for atoms C5 and C6) and C9/C10/C11/C12/S4 (plane *E*, maximum deviation 0.001 Å for atoms C9, C10 and C11). The chelate ring planes (*A* and *C*) are nearly parallel [dihedral angle  $0.7(3)^\circ$ ] and are canted by  $7.0(3)$  and  $8.0(3)^\circ$  with respect to the associated thiophene planes (*D* and *E*). This result differs from that of the Cu<sup>II</sup>–TCT complex, for which the chelate and thiophene planes lie at a dihedral angle of  $17.85^\circ$  (Garcia-Tojal *et al.*, 1999). The Cu<sub>2</sub>S<sub>2</sub> plane *B* is nearly perpendicular to the Cu–TCT chelate planes *A* and *C* (*A/B* and *B/C* dihedral angles are  $81.66(9)$  and  $81.44(9)^\circ$ , respectively), resulting in a zigzag tri-fold arrangement of the fused rings.

## Experimental

The TCT ligand was prepared according to the literature method of Hong *et al.* (2004). The metal complex was prepared through the reaction of [Cu(NCMe)<sub>4</sub>]BF<sub>4</sub> (4.36 g, 13.9 mmol) and TCT (2.57 g, 13.9 mmol) in acetonitrile (80 ml). The resulting yellow solution was

stirred for 30 min at room temperature. The yellow product was precipitated from the solution with the addition of diethyl ether (yield 74.3%). Analysis, calculated for C<sub>8</sub>H<sub>10</sub>BCuF<sub>4</sub>N<sub>4</sub>S<sub>2</sub>: Cu 16.87, C 25.51, H 2.68, N 14.87%; found: Cu 16.92, C 24.04, H 2.68, N 14.03%. X-ray quality crystals of (I) were grown by layering an acetonitrile solution with diethyl ether.

### Crystal data

[Cu<sub>2</sub>(C<sub>6</sub>H<sub>7</sub>N<sub>3</sub>S<sub>2</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>3</sub>N)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>  
*M<sub>r</sub>* = 753.34  
 Orthorhombic, *Pca*2<sub>1</sub>  
*a* = 13.3357 (3) Å  
*b* = 9.1867 (2) Å  
*c* = 22.7980 (5) Å  
*V* = 2793.01 (11) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.792 Mg m<sup>-3</sup>

Cu Kα radiation  
 Cell parameters from 470 reflections  
 $\theta = 3.9\text{--}69.5^\circ$   
 $\mu = 5.40\text{ mm}^{-1}$   
*T* = 100 (2) K  
 Block, yellow  
 0.12 × 0.10 × 0.10 mm

### Data collection

Bruker SMART APEX-II CCD area-detector diffractometer  
 $\omega$  and  $\varphi$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2004)  
*T<sub>min</sub>* = 0.534, *T<sub>max</sub>* = 0.583  
 30209 measured reflections

4947 independent reflections  
 3981 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.088  
 $\theta_{\text{max}} = 69.5^\circ$   
*h* = −15 → 14  
*k* = −10 → 10  
*l* = −27 → 26

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.045  
*wR*(*F*<sup>2</sup>) = 0.111  
*S* = 1.07  
 4947 reflections  
 363 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 ( $\Delta/\sigma$ )<sub>max</sub> = 0.001  
 $\Delta\rho_{\text{max}} = 1.22\text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.36\text{ e \AA}^{-3}$   
 Absolute structure: Flack (1983), with 2291 Friedel pairs  
 Flack parameter: 0.13 (4)

**Table 1**

Selected geometric parameters (Å, °).

Cu1—N7	1.944 (7)	Cu2—S1	2.472 (2)
Cu1—N3	2.031 (6)	S1—C1	1.705 (8)
Cu1—S1	2.327 (2)	S2—C7	1.723 (8)
Cu1—S2	2.463 (2)	N2—C1	1.327 (9)
Cu1—Cu2	2.8094 (15)	N2—N3	1.384 (8)
Cu2—N8	1.929 (7)	N5—C7	1.350 (10)
Cu2—N6	2.051 (6)	N5—N6	1.385 (8)
Cu2—S2	2.313 (2)		
N7—Cu1—N3	133.4 (2)	N6—Cu2—S1	101.33 (18)
N7—Cu1—S1	120.6 (2)	S2—Cu2—S1	108.27 (7)
N3—Cu1—S1	87.43 (18)	Cu1—S1—Cu2	71.59 (6)
N7—Cu1—S2	103.00 (19)	Cu2—S2—Cu1	71.98 (6)
N3—Cu1—S2	101.75 (18)	C1—N2—N3	122.3 (6)
S1—Cu1—S2	108.15 (7)	N2—N3—Cu1	112.5 (4)
N8—Cu2—N6	130.2 (3)	C7—N5—N6	121.9 (6)
N8—Cu2—S2	124.0 (2)	N5—N6—Cu2	113.0 (4)
N6—Cu2—S2	87.36 (18)	N2—C1—S1	123.5 (6)
N8—Cu2—S1	102.9 (2)	C2—C3—S3	124.4 (6)

H atoms were treated as riding, with C—H = 0.96 and 0.93 Å for methyl and vinyl groups, and N—H = 0.86 Å, and with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C,N) for all H atoms. The largest peak in the final difference map lies near the centroid of the Cu<sub>2</sub>/N<sub>6</sub>/C<sub>8</sub>/C<sub>9</sub>/S<sub>4</sub> arc.

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT-Plus (Bruker, 2004); data reduction: SAINT-Plus; program(s) used to

solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *XSHELL* (Bruker, 2004); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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